Electrolytes and Interfaces for Stable High-Energy Na-Ion Batteries

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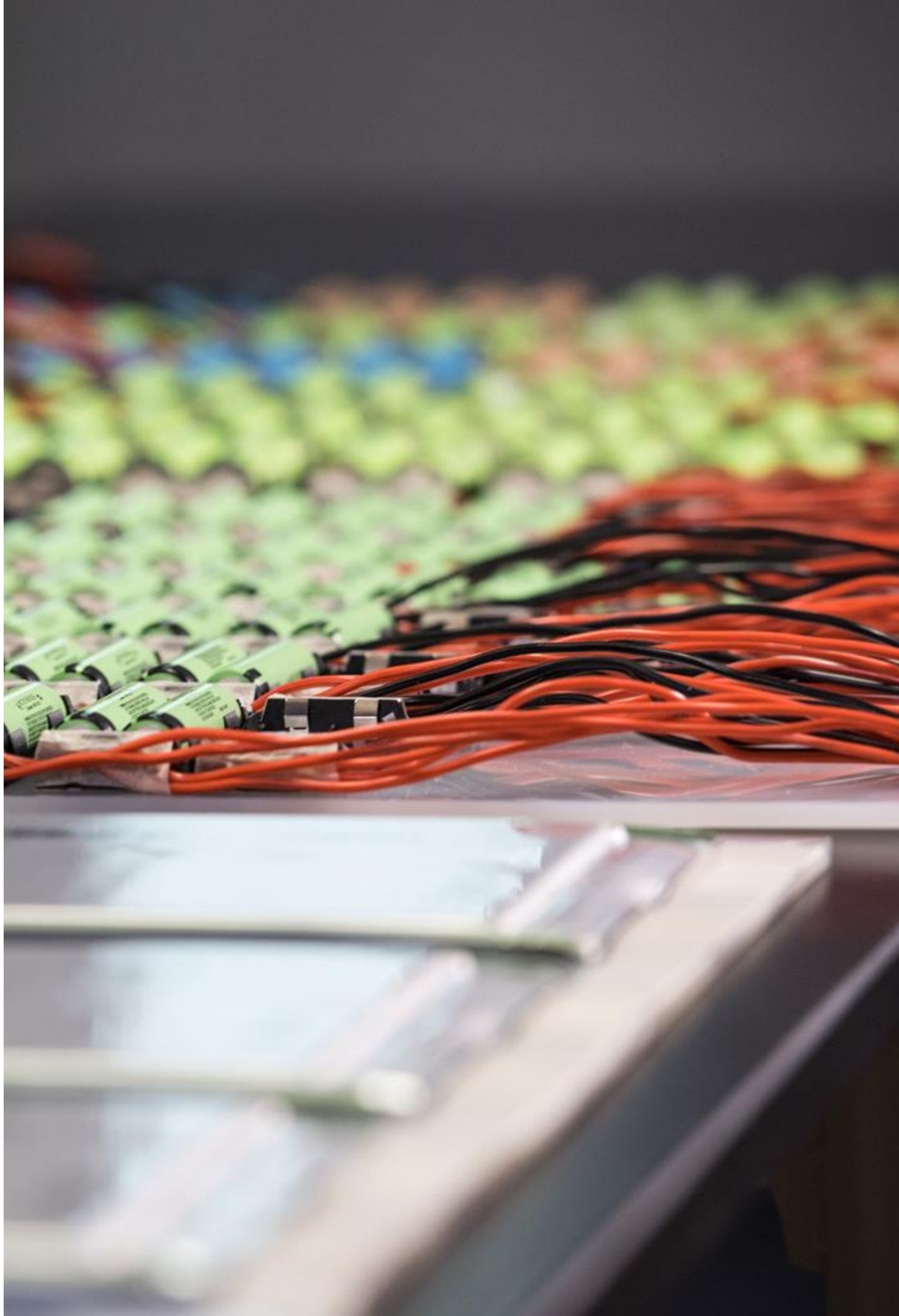

Overview

Timeline

- Start date: Oct. 1, 2018
- End date: Sept. 30, 2021
- Percent complete: 17%

Barriers

- Cost: Need low cost and sustainable anode and cathode material (Co-free) to enable electric vehicle (EV) battery cost < $100/kWh.
- Life: Need functional electrolyte enabling stable electrolyte / electrolyte interface for long cycle life.

Budget

- Project funding
  - DOE share $400K
- Funding for FY19: $400K

Partners

- Argonne National Laboratory
- Lawrence Berkeley National Laboratory

Relevance/Objectives

- Impact
  - Design and understanding of electrolytes and electrolyte/electrode interface in Na-ion battery (NIB) systems is critical for the development of NIB technology as an alternative EV battery solution with lower cost.
- Objective
  - Develop innovative electrolytes and fundamental understanding on the interface between electrode and electrolyte for stable operation of high energy NIB for EV.
    - Improve achievable capacities of NIB electrode materials.
    - Stabilize long cycle life and safe high energy NIBs.
    - Build correlation (electrolyte design rule) between electrochemical performance of Na batteries with the electrolyte/interface properties.

Milestones

Date	Milestones Name/Description	Status
Dec. 31, 2018	Determine the physical-chemical properties of carbonate-based electrolytes and identify the key factor affecting the stability of these electrolytes in Na batteries.	Completed
March 31, 2019	Design new phosphate-based electrolyte with improved electrochemical and thermal stability in Na batteries.	Completed
June 30, 2019	Characterize chemical coordination structure of selected carbonate- and phosphate-based electrolytes for Na batteries.	On track
Sept. 30, 2019	Demonstrate improved capacity, CE and cyclic stability of electrode materials using the electrolytes developed in this work; achieve hard carbon capacity of >250 mAh g^{-1}, ICE >85%, cycle life>200 time.	On track

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Approach

- Identify of the solvent and salt effects for carbonate-based electrolytes to enhance the capacity utilization and coulombic efficiency (CE) of electrode materials for Na batteries.
- Develop new functional nonflammable phosphate-based electrolyte with improved performance of Na batteries.
- Use hard carbon (HC) anode and layered transition metal oxide cathode for electrolyte evaluation.

Coulombic efficiency | **Capacity** | **Cycle Life** | **Rate** | **Safety**

Technical Accomplishments
Conductivity measurement

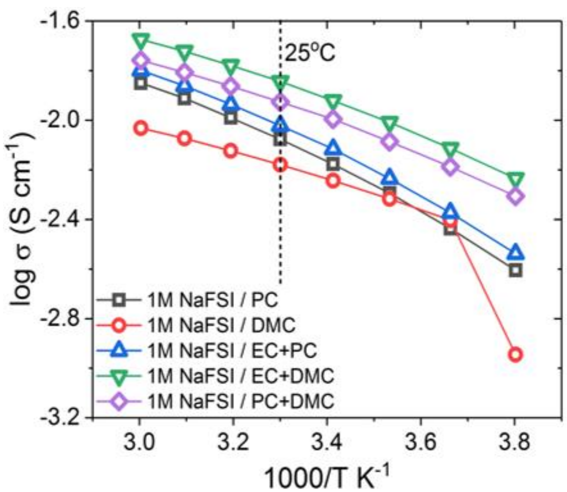
Solvent Effect

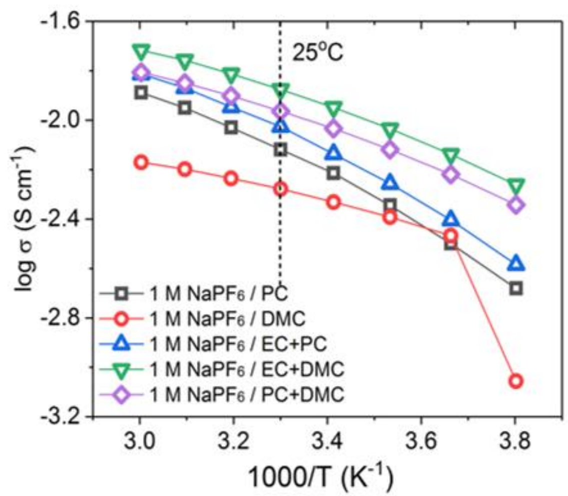
NaFSI salt

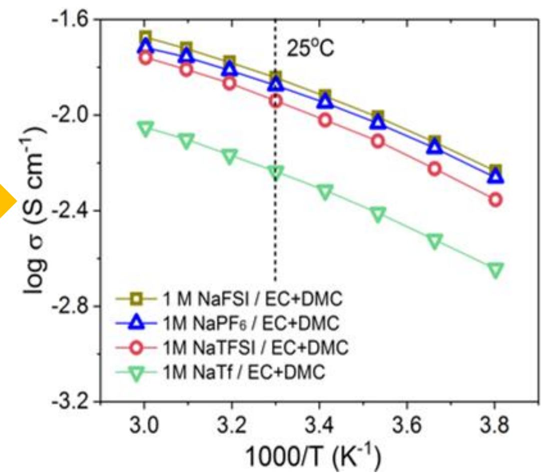
$NaPF_6$ salt

Down Select

Salt Effect





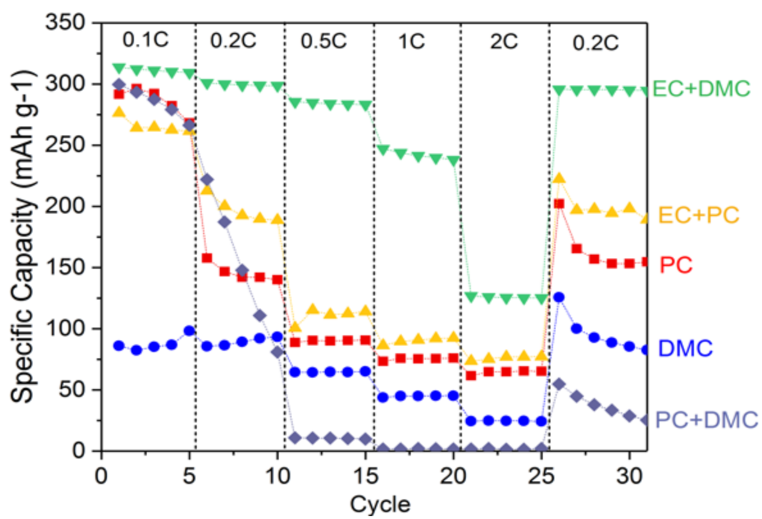


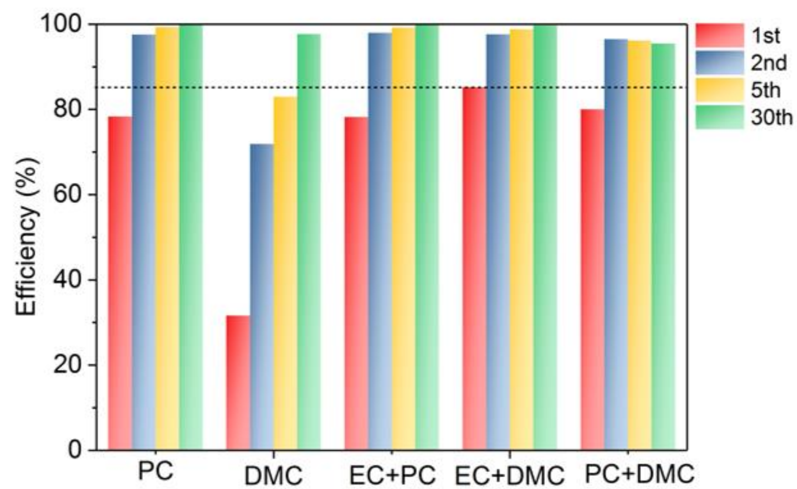
- Solvent Effect → Conductivity sequence: EC+DMC >PC+DMC > EC+PC > PC > DMC
- Salt Effect → Conductivity sequence: NaFSI ~ $NaPF_6$ > NaTFSI > NaTf

EC: Ethylene carbonate; PC: Propylene carbonate; DMC: Dimethyl carbonate

Technical Accomplishments
Solvent effect

1 M $NaPF_6$ in Different Solvents



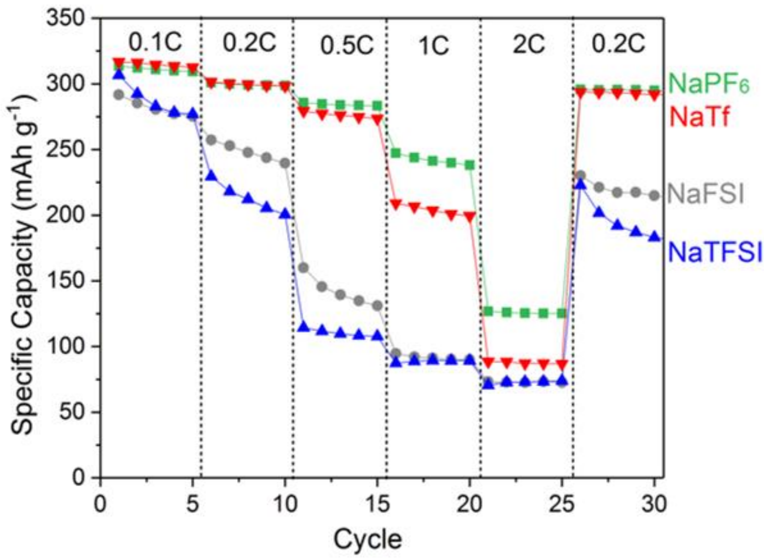


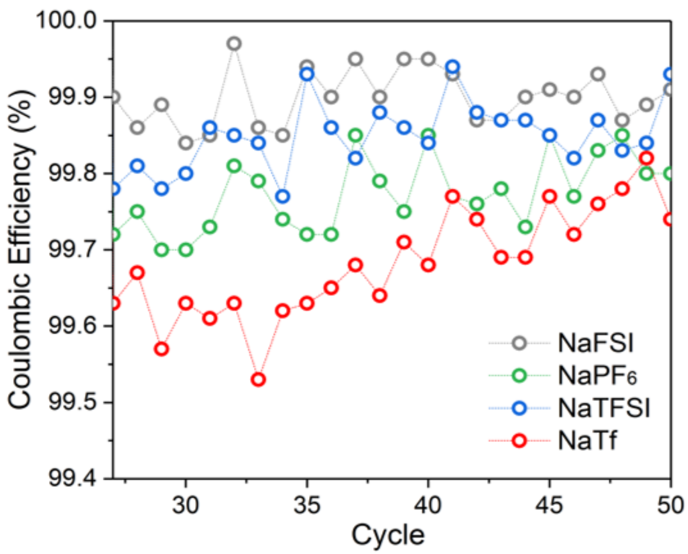
- Solvent has a significant effect on capacity and rate performance of HC anode.
- Co-solvent approach is required to balance CE and rate performance of HC, in which EC is needed for SEI formation with higher coulombic efficiency.
- 1M $NaPF_6$ / EC+DMC exhibits best overall performance.

Technical Accomplishments

Salt effect

Different Salt in EC +DMC co-solvent



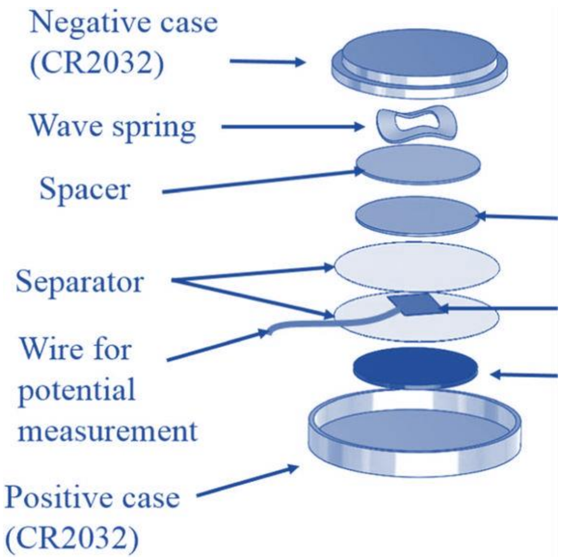


- **For CE**: NaFSI > NaTFSI > $NaPF_6$ > NaTf
- **For capacity**: $NaPF_6$ > NaTf > NaFSI > NaTFSI
- **For Rate**: $NaPF_6$ > NaTf > NaFSI> NaTFSI

Note: HC‖Na Half cells was used for the primary evaluation of electrolytes.
HC electrode: HC:PVDF:CB=90:5:5, mass loading: 2-3 mg/cm^2

Technical Accomplishments

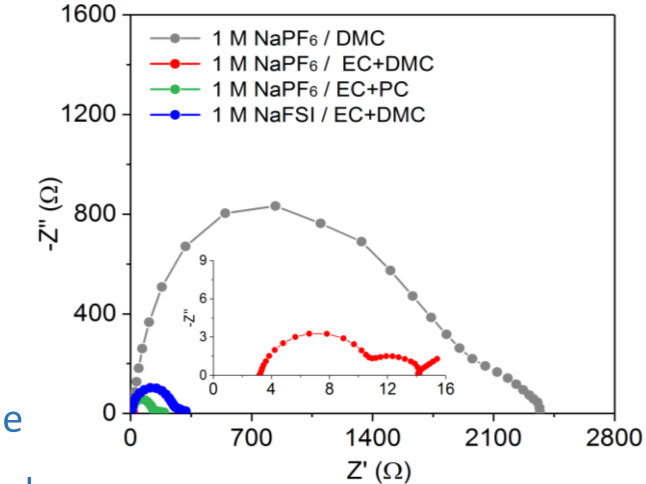
Three-electrode electrochemical impedance measurement

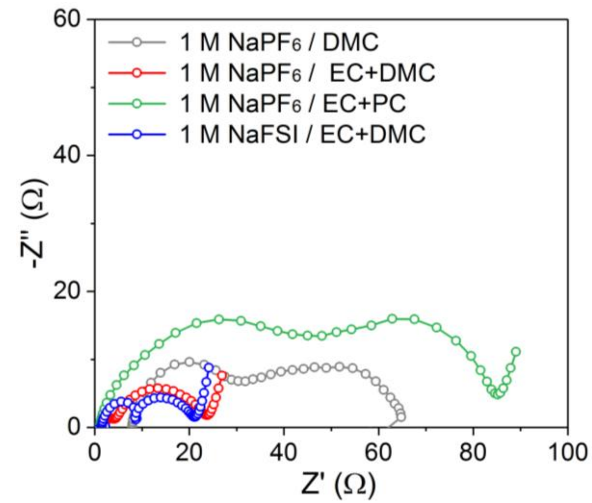


Na metal Counter electrode

Na metal Reference electrode

Hard Carbon Working electrode



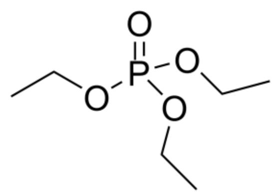


- 1 M $NaPF_6$ / EC+DMC exhibits lowest impedance on both hard carbon and Na metal anode.
- EC is important to form stable SEI layer on both HC and Na metal.

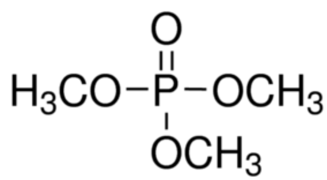
Technical Accomplishments

Functional phosphate-based electrolyte

Triethyl phosphate (TEP)

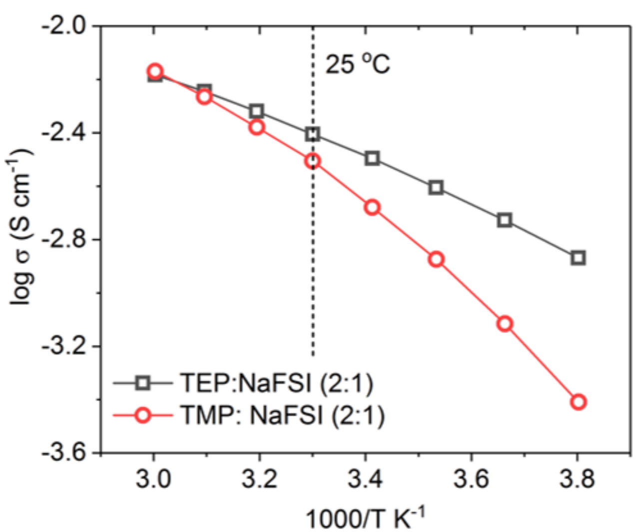


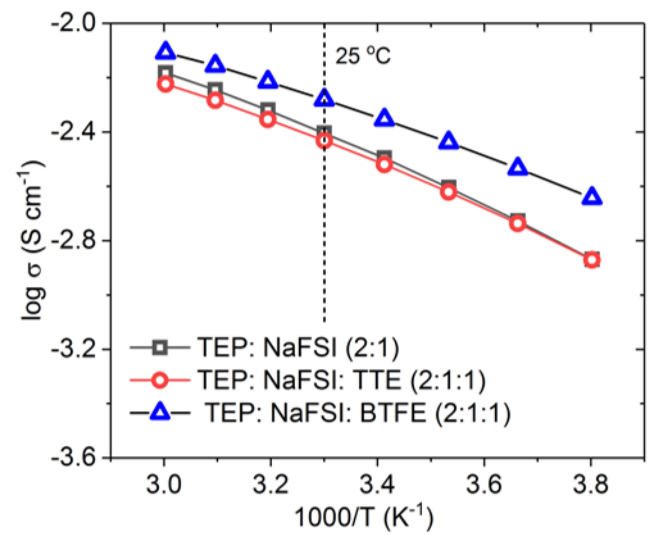
Trimethyl phosphate (TMP)



- ✓ High oxidization window
- ✓ High thermal stability
- ✓ Nonflammable

Molar Ratio: 1) TEP: NaFSI (n=1, 2, 4, 8)
2) TMP: NaFSI (n=1, 2,4, 8)
3) TEP: NaFSI: TTE
4) TEP: NaFSI: BTFE



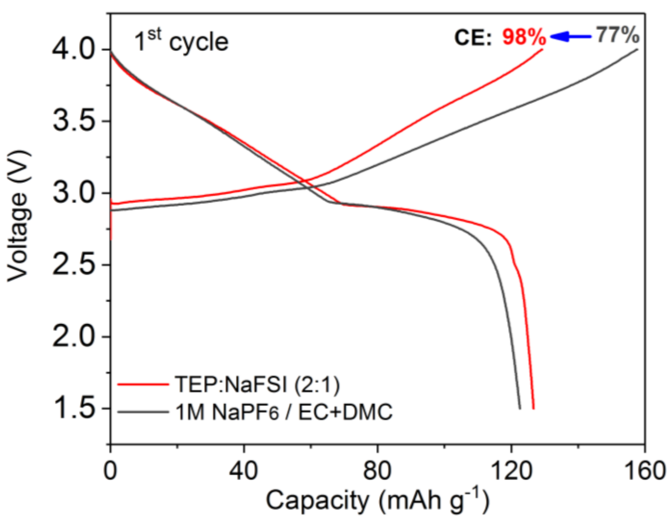


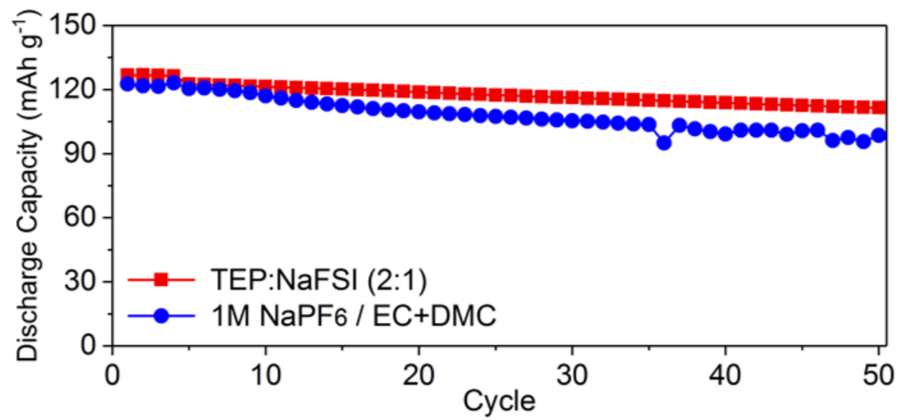
- Nonflammable phosphate-based electrolytes show an ionic conductivity ~4 mS cm^{-1} at RT.

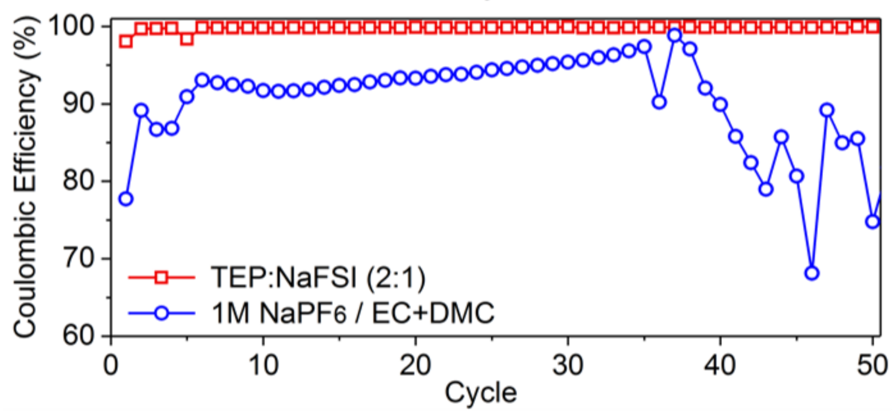
Technical Accomplishments

Functional phosphate-based electrolyte – cathode stability test

High compatibility with Na Cathode





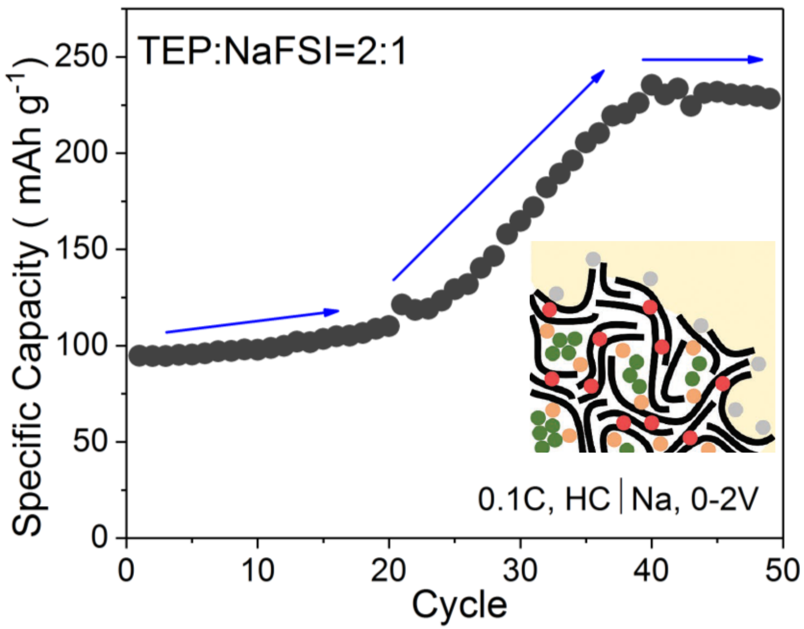


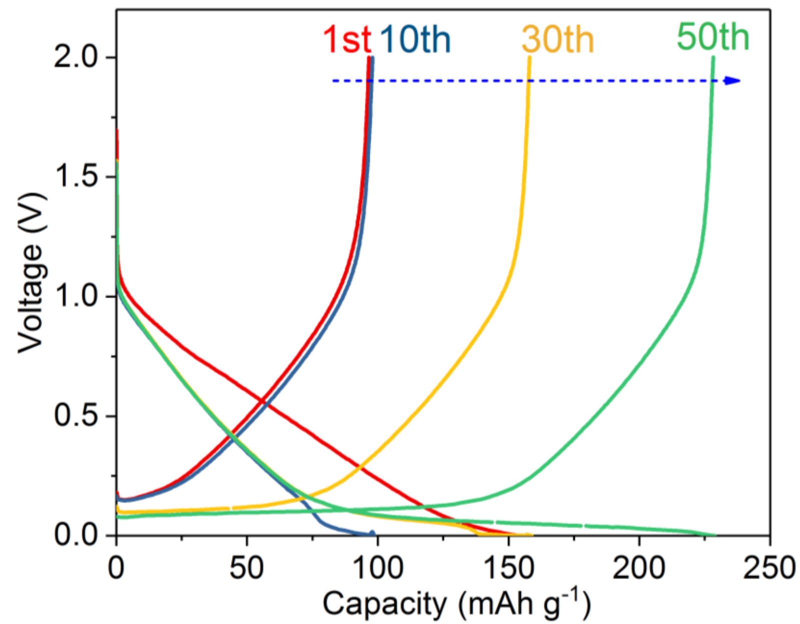
- TEP-based electrolyte is more compatible with cathode than conventional carbonate electrolyte, with greatly improved coulombic efficiency and available capacity.

Note: Na ‖ O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ half cell was used to evaluate for phosphate electrolyte. Loading: ~16 mg/cm^2

Technical Accomplishments

Functional phosphate-based electrolyte – anode stability test





- Na‖HC cells needs long time to activate the capacity from low discharge plateau of HC in the phosphate-based TEP:NaFSI (2:1) electrolyte.
- Pre-formation process may need to be used to condition anode.

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Technical Accomplishments

- Completed the carbonate-based electrolyte composition (salt, solvent) optimization for hard carbon anode.
- Designed new functional phosphate-based electrolytes for NIB cathode with high compatibility.
- Designed *in-situ* three-electrode EIS measurement to identify the electrode process at cathode/anode interface individually.

Collaboration and Coordination

- Dr. Chongmin Wang (PNNL) for TEM and STEM images etc.
- Dr. Mark Engelhard (PNNL) for XPS analysis.
- Prof. Yong-Sheng Hu (Institute of Physics, Chinese Academy of Sciences) for providing Na ion cathode material electrodes.

Remaining Challenges and Future Work

Key Challenges

- The poor wetting problems of sodium ion electrolyte with convectional PP/PE separator.

- The compatibility of electrolyte for cathode and anode.

- Availability of benchmark cathode materials & electrodes for sodium ion batteries electrolyte evaluation.

Future Work

- Characterize chemical coordination structure of selected carbonate- and phosphate-based electrolytes for Na batteries.

- Optimize electrolyte additives to tailor the solvation clusters in electrolyte to improve their electrochemical performance and wettability on separator.

- Use full cell configuration to evaluate the optimized electrolyte.

Any proposed future work is subject to change based on funding levels.

Summary

- The screening of electrolyte component (salt, solvent) has been completed for NIBs. EC is critical to both hard carbon anode and Na metal to form stable SEI in carbonate-based electrolytes for NIBs.
- Nonflammable phosphate-based electrolytes show high compatibility with layered O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ cathode material with the first cycle CE improved from 77% to 98%.
- Next step will focus on understanding molecular solvation structures and SEI formation on HC and $NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ cathode to further improve the electrochemical behavior to NIBs full cell.

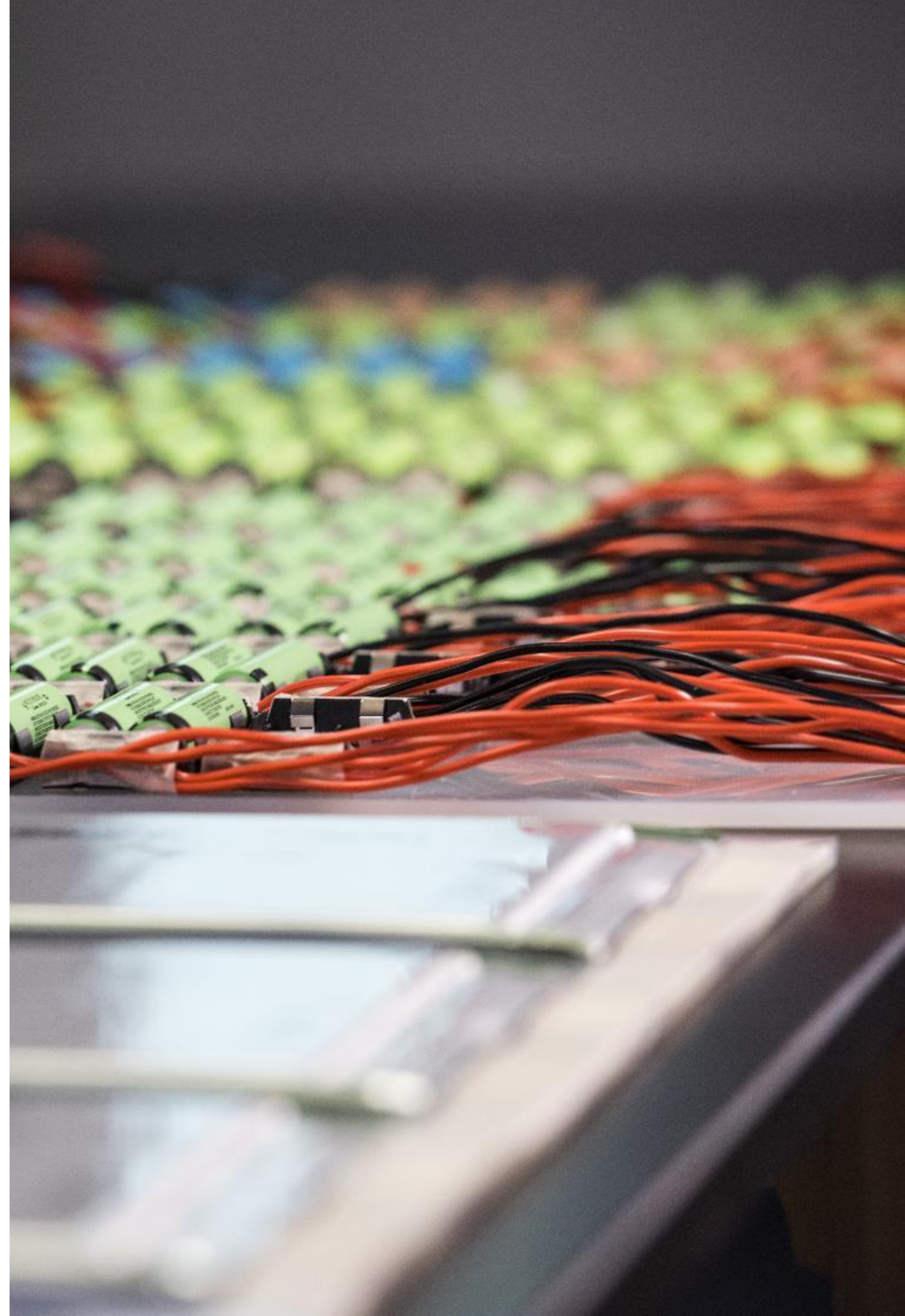
Acknowledgement

- Support form DOE/VTO/BMR program is greatly appreciated.

- Team member:

  Phung M Le, Thanh D Vo, Yan Jin, Noha Sabi, Ji-Guang Zhang

Technical Backup Slides



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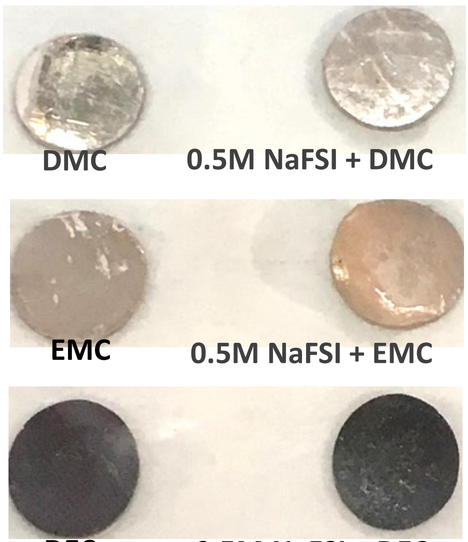
Na metal stability Test

Store Na metal in solution for 7 days



- Electrolyte is more easy to react with Na metal than solvent itself.

Solution	Chemical stability with Na metal
EC	√ √ √
PC	√ √ √
DMC	√ √ √
EMC	×
DEC	× ×
0.5 M NaFSI + EC	√ √
0.5 M NaFSI + PC	√ √
0.5 M NaFSI + DMC	√ √
0.5 M NaFSI + EMC	× ×
0.5M NaFSI + DEC	× × ×

VTF Equation of ionic conductivity

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_a}{R(T - T_0)}\right)$$

R is the universal gas constant and the constants σ_0 (S cm^{-1}), E_a (J mol^{-1}), and T_0 (K) are adjustable parameters.

- **Carbonate-based Electrolyte**

Electrolyte	E_a (J. mol^{-1})
PC + 1M NaFSI	2681
DMC + 1M NaFSI	2070
EC-PC + 1M NaFSI	2194
EC-DMC + 1M NaFSI	1994
PC-DMC + 1M NaFSI	2220
PC + 1M $NaPF_6$	2754
DMC + 1M $NaPF_6$	1637
EC-PC + 1M $NaPF_6$	2245
EC-DMC + 1M $NaPF_6$	**1924**
PC-DMC + 1M $NaPF_6$	2143

- **Phosphate-based Electrolyte**

Electrolyte	E_a (J. mol^{-1})
TEP:NaFSI = 2:1	2507
TMP:NaFSI = 2:1	4196
TEP:NaTFSI:TTE= 2:1:1	2357
TEP:NaTFSI:TTE = 2:1:2	2698
TEP:NaTFSI:TTE = 2:1:0.5	3169
TEP:NaTFSI:BTFE= 2:1:1	1944
TEP:NaTFSI:BTFE = 2:1:2	1695

Note: The activation energy of electrolytes was fitting using VTF function for the ionic conductivity measurement results in page 6 and 10.

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Critical Assumptions and Issues

- Na-ion battery technology will be a competitive alternative choice for electric vehicles.
  - The crustal abundance of sodium is far greater than that of lithium; Sodium supply is sustainable with low cost.
- State-of-the-art anode material for Na-ion batteries
  - Hard carbon could be the #1 choice for state-of-the-art anode at the current stage due to safety, cost and reliability advantages.
  - This project uses hard carbon as the anode to evaluate the electrolyte.
- State-of-the-art cathode for Na-ion batteries
  - Co-free cathode with earth abundant element such as Fe, Mn, could further reduce the cost of battery cost.